

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE MAY 1997		3. REPORT TYPE AND DATES COVERED Final Report 2/15/94 to 2/14/97
4. TITLE AND SUBTITLE  LINEAR ORGANOSILICONE STRUCTURES WITH DELOCALIZED $\sigma$ BONDS			5. FUNDING NUMBERS  DAAH04-94-G-0018	
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 31420.6 -CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  <b>Results - Highlights.</b> (i) The generally accepted textbook notion of gauche and anti conformer arrangements about each single bond in a linear saturated chain needs to be revised in that a third conformer (ortho) exists within a certain range of lateral substituent sizes. (ii) Electronic excitation in linear all-anti permethylated silicon chains is localized in a single SiSi bond if the chain is six silicon atoms long or shorter and delocalized over all SiSi bonds if the chain has seven or more silicon atoms. (iii) In a twisted conformer of $\text{Si}_7\text{Me}_{16}$ , excitation is localized, and this conformer interconverts adiabatically with the all-anti conformer. (iv) The chains in which				
(continued on reverse side) <b>DETO QUALITY INSPECTED 4</b>				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	

FINAL REPORT

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MAY 1997

U.S. ARMY RESEARCH OFFICE

DAAH04-94-G-0018

UNIVERSITY OF COLORADO

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## 1. STATEMENT OF THE PROBLEM STUDIED:

The aim of our work was twofold: (i) to understand the ground state structure of the conformers of oligosilane chains, and in particular, to define the scope of the unexpected discovery of ortho conformers, and (ii) to separate and understand the individual spectroscopic and photophysical properties of these conformers.

## 2. SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS:

(i) *Ground-State Conformations.* We have found that in addition to the usually recognized gauche and anti arrangements around a single bond, with SiSiSiSi dihedral angles  $\omega$  of about  $60^\circ$  and about  $165^\circ$ , respectively, ortho arrangements with  $\omega = 90^\circ$  should also be present in methylated oligosilane chains. The existence of this new type of conformer is due to van der Waals interactions between substituents in positions 1 and 4, and is predicted only for a certain range of substituent sizes, such as methyl on silicon or fluorine on carbon.

We have published three detailed matrix isolation studies of spectral properties of individual conformers, interpreted in terms of ab initio quantum chemical calculations. This work was done for  $\text{Si}_4\text{H}_{10}$ ,  $\text{Si}_4\text{Me}_{10}$ , and  $\text{C}_4\text{F}_{10}$ . For the first two, both infrared and uv-visible spectra were obtained, for the last one, only infrared spectra. For  $\text{Si}_4\text{Me}_{10}$ , matrix isolation Raman spectra were also obtained. In  $\text{C}_4\text{F}_{10}$ , three conformers were identified spectrally, gauche, ortho, and anti. This was the first spectral identification of an ortho conformer ever. The results for  $\text{Si}_4\text{H}_{10}$  and the related  $\text{Si}_3\text{H}_8$  are particularly significant for investigations of chemical vapor deposition of amorphous silicon, where such species are suspected to occur as intermediates.

Predictions for numerous kinds of linear polymers have been made. Often, the number of conformers is much larger than previously suspected. For example, in  $\text{Si}_5\text{Me}_{12}$  we already expect eight pairs of enantiomeric conformers, and the number increases rapidly as the chain length increases. The results are significant for the understanding of properties of linear polymers of all kinds, since many are expected to have ortho conformers. This is important since properties of linear polymers are greatly affected by the conformational behavior of their backbones.

(ii) *Photophysics.* The investigation of the electronic properties of floppy chains is complicated immensely by the large number of conformers typically present in a sample. Our investigation therefore included oligosilanes constrained to a single conformation by synthetic design. Thus, we were able to study chain conformations one at a time using artificially introduced constraints. In one series of experiments, we investigated tetrasilanes confined to small dihedral angles by having their ends joined with a short alkane chain, in another, we introduced the new concept of chain racking, in which a normally floppy chain molecule is attached at both ends to alkane chains, which are then stretched between the ends of a rigid-rod molecule that serves as a torture rack and restricts the chain conformation to the all-anti form. These approaches permitted us to confirm the previous suspicion that it is not the tetrasilane transition energy but its transition intensity that changes with the conformation, to discover a new excited state of this molecule, and to identify without doubt which of the conformers of permethylated hexasilane is the most stable, and which one fluoresces. The tetrasilane results were accounted for by relatively simple theory, and this was checked by state-of-art calculations. The results also provided information about orbital energies in the tetrasilanes from their photoelectron spectra, which are interpretable in terms of simple theory, and about the photochemical chain abridgement

reaction.

The studies that have been completed have considerably improved the understanding of electronic excitation in saturated systems in general, and have clear relevance for the properties of materials such as amorphous silicon. They revealed a rich landscape of coexisting localized and delocalized fluorescent  $\sigma\sigma^*$  excited state isomers, as well as excited isomers that differ only by the location of the SiSi bond in which electronic excitation is localized. Adiabatic conversion of one excited isomer into another was found to be common. Briefly stated, the  $\sigma\sigma^*$  excitation in the SiSi backbone is localized in a single SiSi bond if the chain is short, and delocalized over all the SiSi bonds present if the chain is long. For the all-anti conformer, localization in the relaxed excited state geometry is observed up to and including six silicon atoms in the chain, delocalization is observed from seven silicon atoms higher.

For twisted chains, the usual concept of  $\sigma\sigma^*$  excitation of the silicon chain is inaccurate, as configuration interaction with  $\sigma\pi^*$  type excitation is very important. This finding permitted a reinterpretation of the conformational dependence of the electronic excitation in tetrasilane. It has now been verified beyond doubt that the first singlet excitation energy is very nearly the same for the gauche and the anti conformer, much against earlier beliefs. The reason for the mistaken traditional concept is the weakness of the first absorption band of the gauche species. The high-energy peak that was actually observed a long time ago belongs to a higher excited state. The situation is readily understood and accounted for in theoretical terms. In this context, we have studied the effect of the inclusion of diffuse functions in a calculation of excited state wave functions, in a free molecule and in a molecule surrounded by a matrix environment. We found that in the matrix environment, the lowest excited states of tetrasilane are of valence nature and do not require Rydberg functions for a reasonable description. This is essential for any efforts to describe the electronic excitation in terms of simple models, whose use is important for the treatment of polymers.

For silicon chains from  $\text{Si}_4\text{Me}_{10}$  to  $\text{Si}_{10}\text{Me}_{22}$ , we measured the absorption, emission, and excitation spectra, the fluorescence quantum yield, and the time-resolved fluorescence decay from room temperature down to 30 K. Quantitative modeling of the kinetics is very complicated and not quite finished, but the results are qualitatively clear. As indicated above, the emitting state changes its nature from self-trapped exciton in chains with six or fewer silicon atoms, where the excitation resides on a single stretched SiSi bond, to delocalized exciton in chains with eight or more SiSi bonds, where all SiSi bond lengths are roughly equal. Dual emission is observed in  $\text{Si}_7\text{Me}_{16}$ , where both types of excitation correspond to minima in the excited state potential energy surface, the delocalized one in the all-anti conformer, and the localized one in a twisted conformer. At very low temperatures, only the more stable all-anti conformer is present in the sample and only the delocalized excited state is produced upon irradiation. However, at other temperatures, twisted conformers are present as well, and one of them emits from a localized excited state upon irradiation, and dual emission is then observed. The two fluorescent conformers interconvert at higher temperatures and are at quasi-equilibrium.

A very exciting result is the new observation that there is dual emission even in the six-silicon and five-silicon chains. It is due to the anti conformer of the former and the anti, anti conformer of the latter. Both emissions are from localized excitons, and are assigned to states in which one or another SiSi bond in the molecule is stretched. At very low temperatures, the

excitation is trapped in one bond, at higher temperatures it moves to another bond. At intermediate temperatures, both emissions are observed. Such "excitation-location" isomerism, or "bond-stretch" isomerism, in an electronically excited state of a small molecule is novel. The structure of the localized  $\sigma\sigma^*$  lowest excited state of  $\text{Si}_4\text{H}_{10}$  was deduced from a CASSCF minimization of excited state geometry. It was found that the central bond is about 0.2 Å longer when it is excited than when it is in the ground state. These results have general implications. Delocalization in a linear system is limited not only in chains that are too long, but also in those that are too short.

### 3. MANUSCRIPTS SUBMITTED OR PUBLISHED:

1. Teramae, H.; Michl, J. "Electronic States of Linear Tetrasilane and Polysilanes", *Mol. Cryst. Liq. Cryst.*, **1994**, 256, 401.
2. Albinsson, B.; Michl, J. "The Gauche, Ortho, and Anti Conformers of Perfluoro-*n*-butane: Matrix-Isolation IR Spectra", *J. Am. Chem. Soc.*, **1995**, 117, 6378.
3. Albinsson, B.; Teramae, H.; Downing, J.; Michl, J. "Conformers of Saturated Chains: Matrix Isolation, Structure, IR and UV Spectra of *n*-Si<sub>4</sub>Me<sub>10</sub>", *Chem. Eur. J.*, **1996**, 2, 529.
4. Albinsson, B.; Michl, J. "The Anti, Ortho, and Gauche Conformers of Perfluoro-*n*-Butane: Matrix-Isolation IR Spectra and Calculations", *J. Phys. Chem.*, **1996**, 100, 3418.
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6. Imhof, R.; Antic, D.; David, D. E.; Michl, J. "Conformational Effects in Photoelectron Spectra of Tetrasilanes", *J. Phys. Chem.*, in press.
7. Imhof, R.; Teramae, H.; Michl, J. "Conformational Effects in UV Absorption Spectra of Tetrasilanes", *Chem. Phys. Lett.*, in press.
8. Mazières, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. "[2]Staffane Rod as a Molecular Rack for Unravelling Conformer Properties: Proposed Singlet Excitation Localization Isomerism in *anti,anti,anti*-Hexasilanes", *J. Am. Chem. Soc.*, in press.
9. Neumann, F.; Teramae, H.; Downing, J. W.; Michl, J. "Gauche, Ortho, and Anti Conformations of Saturated A<sub>4</sub>X<sub>10</sub> Chains: When Will all Six Conformers Exist?", submitted for publication.
10. Teramae H.; Michl, J. "Geometry of the Localized  $\sigma\sigma^*$  Excited State of *n*-Tetrasilane", submitted for publication.
11. Teramae, H.; Antic, D.; Michl, J. "Calculation of the Conformational Dependence of Electronic Excitation in Tetrasilane", submitted for publication.
12. Raymond, M. K., "The Photophysics of Permethylated Polysilane Chains," *Ph. D. Dissertation*, University of Colorado, Boulder, CO, 1997.

**4. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:**

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**5. INVENTIONS:**

None.

**6. TECHNOLOGY TRANSFER:**

None.

## 200-word abstract:

**Results - Highlights.** (i) The generally accepted textbook notion of gauche and anti conformer arrangements about each single bond in a linear saturated chain needs to be revised in that a third conformer (ortho) exists within a certain range of lateral substituent sizes. (ii) Electronic excitation in linear all-anti permethylated silicon chains is localized in a single SiSi bond if the chain is six silicon atoms long or shorter and delocalized over all SiSi bonds if the chain has seven or more silicon atoms. (iii) In a twisted conformer of  $\text{Si}_7\text{Me}_{16}$ , excitation is localized, and this conformer interconverts adiabatically with the all-anti conformer. (iv) The chains in which excitation is localized exhibit isomerism of a new type, in which the isomers differ by the location of the stretched bond in which the excitation is localized (stretched bond isomerism). Upon thermal activation, the less stable isomers convert adiabatically to the more stable ones. (v) The usual notion that the lowest singlet electronic excitation energy of an oligosilane strongly depends on conformation is incorrect, at least in the case of decamethyltetrasilane. It is the intensity and not the energy that is exquisitely sensitive to conformation. This is due to the presence of an avoided crossing between configurations that go to  $\sigma\sigma^*$  and  $\sigma\pi^*$  limits, respectively, at planar geometry.